

# Electrostatic Energy Calculations for Molecular Dynamics

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The evaluation of Coulomb forces is a difficult task. The summations that are involved converge only conditionally and care has to be taken in selecting the appropriate procedure to define the limits. The Ewald method is a standard method for obtaining Coulomb forces, but this method is rather slow, since it depends on the square of the number of atoms in a unit cell. In this paper we have adapted the plane-wise summation method for the evaluation of Coulomb forces. The use of this method allows for larger computational cells in molecular dynamics calculations.

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## **I. Introduction**

When periodic boundary conditions are employed, a molecular dynamics (MD) computational cell containing  $N$  atoms may be considered to be a unit cell with an  $N$ -point basis in a crystal lattice. The calculations of long-range Coulomb interactions can then be performed with techniques developed for the evaluation of electrostatic energies and forces within crystals. While essentially all molecular dynamics simulations which include long-range ionic interactions have used the Ewald method<sup>1</sup> to calculate the Coulomb energy and forces, alternative methods offer some computational advantages. In the following sections, calculations of lattice sums with Ewald, planewise summation, and multipole techniques are briefly described and compared. The convergence properties of the Ewald summation are shown to be due to effective surface charges included implicitly in the sum and a multipole formulation is presented which produces results identical to those obtained with the Ewald method.

## **II. Lattice summation methods**

In the Ewald method, the potential due to a lattice of unit point positive charges is obtained by surrounding each point charge with equal positive and negative Gaussian charge distributions and a uniform negative volume charge. For negative charges one simply reverses the signs of all charges. The point charges plus the negative Gaussian distributions and the positive Gaussian distributions plus the negative volume charges are then summed separately, with the convergence of the positive Gaussian-volume charge lattice sum improved by performing the sum in reciprocal space.

When the energy of a collection of positive and negative point charges in the unit cell of a neutral crystal is calculated using the Ewald potential, the background charges

cancel in the volume of the crystal and the energy sum is generally taken to be that due to the point charges alone.

The overall speed of convergence for Ewald sums can be improved in a simple way by adjusting the free parameter in the equations so that the direct and reciprocal sums converge at the same rate. Nijboer and de Wette<sup>2</sup> have shown that this will occur if  $\alpha = \sqrt{\pi}/L$ , where  $L$  is the length of a cubic cell edge and  $\alpha$  is the free parameter. Sangster and Dixon<sup>3</sup> show that the reciprocal sum can be reformulated so that the number of terms is proportional to  $N$  rather than  $N^2$ , and the free parameter can then be adjusted to increase the number of reciprocal space terms and decrease the number of direct space terms required to obtain a given degree of convergence. The optimum value of  $\alpha$  will be that which minimizes the overall computational time. An implementation of both the original and modified Ewald methods<sup>4</sup> indicates that the techniques suggested by Sangster and Dixon can increase the speed of computation by a factor of about two or three.

A drawback of using the Ewald method for computing Coulomb forces presents itself when simulations containing large numbers of particles are considered. For an MD cell containing  $N$  atoms, the number of Ewald sums required to calculate the forces is proportional to  $N^2$ . The terms which are summed in an Ewald energy calculation are rather complicated, particularly the direct sum. A force calculation requires the calculation and summation of terms which are even more complicated, and the repeated calculations of lattice sums in a molecular dynamics calculation can be very time consuming,

An alternative method for performing Coulomb lattice sums is the planewise summation method (PSM) first developed by Nijboer and de Wette<sup>5</sup> for dipole lattices and

crystals with monoclinic and higher symmetry. In this method, lattice summations are computed by applying a two-dimensional Fourier transform over two indices and then performing the summation over the third index analytically. There are no additional charges introduced to speed the convergence.

The PSM was later extended to include summation of multipole lattices of all orders<sup>6</sup>, summation of multipole lattices in triclinic crystals<sup>7</sup>, and the direct calculation of the electrostatic potential<sup>8</sup>.

The planewise summation method offers some computational advantages over the Ewald method. The lattice summation is performed over two indices rather than three, there is only a reciprocal space sum and not a direct sum, and the individual terms in the sum are generally simpler to calculate than those in an Ewald sum.

The number of calculations required to find the electrostatic energy by direct planewise summation is proportional to  $N^2$ . An additional disadvantage of the direct planewise method is the conditional convergence of the lattice sums, leading to a dependence of the total energy on the choice of the planes in the crystal and inconsistency with periodic boundary conditions when the dipole moment of the unit cell is nonzero.

The conditional convergence of the PSM is due to the general convergence properties of the Coulomb lattice sum for a neutral unit cell. The energy sum may be written:

$$E_{coul} = \frac{e^2}{2} \sum_{\alpha=-\infty}^{\infty} \sum_{\beta=-\infty}^{\infty} \sum_{\gamma=-\infty}^{\infty} \sum_{i=1}^N \sum_{j=1}^N ' \frac{q_i q_j}{|\vec{r}_i - \vec{R}_{\alpha\beta\gamma} - \vec{r}_j|} \quad (1)$$

where  $\vec{R}_{\alpha\beta\gamma} \equiv \alpha\vec{a} + \beta\vec{b} + \gamma\vec{c}$ ;  $\vec{a}$ ,  $\vec{b}$ , and  $\vec{c}$  are Bravais lattice vectors;  $q_i$  is the valence of the  $i^{th}$  atom; and the prime on the summation over lattice indices indicates omission of the terms for which  $i = j$  and  $\alpha = \beta = \gamma = 0$ .

Using this expression to approximate the energy by evaluation of a finite number of terms leads to contradictions with the periodic boundary conditions which are commonly imposed on a MD cell. In the usual case of a cell in which the total charge is zero, the energy sum will approach a finite limit. However, if the cell has a nonzero dipole moment there will be a constant electric field component throughout the MD cell, so that the potential at a point on one face of the cell will differ from that at a point translated through the cell along a Bravais lattice vector to the opposite face. The existence of a non-zero dipole moment also makes the constant electric field component dependent on the choice of the unit cell. An example of how this can occur is illustrated in Figure 1. Two different, equivalent choices for the unit cell of a tetragonal  $AB_2$  ionic compound are shown along with the net dipole moment for the unit cell. It is seen that the dipole moment changes sign if the locations of the atoms on the corners of the cell are redefined. If the derivative of the energy sum is calculated for each of these cells, then each sum will contain terms describing an electric field parallel to the dipole moment of the associated unit cell, and even though the cells are physically equivalent the electric fields for the two cases will differ in sign.

In an MD simulation with periodic boundary conditions, if a particle leaves the unit cell then there is an identical particle which simultaneously enters the cell through the opposite face. If the exiting particle is replaced in the energy sum by the entering particle, the unit cell is effectively redefined. The configuration of the unit cell could change, for example, from one of those shown in Figure 1 to the other in the course of the simulation. When this happens, the electric field inside the cell changes discontinuously. Since the particles in an MD cell are not taken to have any particular symmetry, a

dipole moment is generally present and discontinuities in the electric field and therefore the forces is the general rule.

The dependence of the energy sum on the dipole moment of the unit cell is well known. In addition to early studies on the effect of the order of summation of terms on the energy totals<sup>9</sup>, the development of fast summation techniques for the Coulomb energy of ionic lattices has led to methods which can give different total energy values for the same unit cell. The Ewald method and the planewise summation method, for example, yield different values if the unit cell has a net dipole moment.

An alternative to both the Ewald and the planewise method as discussed above begins with the separation of the Coulomb potential into multipoles. The resulting multipole lattice sums can then be summed by the planewise method. The lattice sums do not contain the atomic positions, so if simulations are carried out in a unit cell with fixed shape, these sums are constant and need to be calculated only once. For simulations in MD cells with variable shape, the lattice sums must be recalculated at each time step. In either case, using procedures similar to those of the fast multipole method of Greengard and Rokhlin<sup>10</sup> it is possible to construct algorithms for the forces which require a number of calculations proportional to  $N$ .

Although a multipole expansion of the Coulomb energy contains the same indeterminacy and dipole dependence of the direct Coulomb sum, a simple modification can be made which results in lattice sums which are all absolutely convergent and which gives results identical to those obtained by the Ewald method. In the next section, the Ewald energy sum is derived as the limit of a finite lattice summation, and the magnitude of the implicit surface charges is found. The following section describes the modified multipole

formulation and shows the equivalence of this method to the Ewald method.

### III. The Ewald Method for Finite Lattices

Since Ewald lattice sums are absolutely convergent while direct Coulomb lattice sums can be conditionally convergent, there must be contributions to the Ewald sums in addition to those from the original point charges and their images. By replacing the infinite lattice summation in the Ewald method with a summation over a very large but finite lattice, the additional terms can be expressed as surface charges located on the faces of the volume occupied by the lattice.

The Ewald potential includes a sum of terms from point charges, positive and negative Gaussian charge distributions, and a uniform background charge. The Gaussian distributions cancel at each lattice point, so the electrostatic potential at a point  $\vec{r}$  is due only to a lattice of unit point charges plus a neutralizing background charge. This potential is:

$$\Phi_{ew}(\vec{r}) \equiv \lim_{M \rightarrow \infty} \sum_{\alpha\beta\gamma=-M}^M \left\{ \frac{1}{|\vec{R}_{\alpha\beta\gamma} - \vec{r}|} - \frac{1}{V} \int_{V_{\alpha\beta\gamma}} d^3r' \frac{1}{|\vec{R}_{\alpha\beta\gamma} + \vec{r}' - \vec{r}|} \right\} \quad (2)$$

$V$  is the volume of the unit cell and  $V_{\alpha\beta\gamma}$  is the volume around the lattice point  $\vec{R}_{\alpha\beta\gamma}$ . In order to simplify the expression for the potential, the limits of the summations are taken to be the same for all three directions. The lattice sum converges with increasing  $M$ , although the value of the sum depends on the manner in which the limits are approached and will be different if we take the limits  $M_\alpha, M_\beta, \text{ and } M_\gamma$  in a different way.

When the energy of a collection of positive and negative point charges in the unit cell of a neutral crystal is calculated using the Ewald potential, the background charges cancel in the volume of the crystal. There are, however, regions on the surfaces of a finite

lattice in which the overlapping volume charges do not cancel. The magnitude of these charges is found by consideration of the volume charge contribution to the electrostatic energy sum.

The electrostatic energy in the Ewald formulation is equal to

$$\begin{aligned}
E_{ew} &= \frac{e^2}{2} \sum_{i=1}^N \sum_{j=1}^N \Phi_{ew}(\vec{r}_i - \vec{r}_j) \\
&\equiv E_{coul} + E_{surf}^{(ew)} \\
E_{coul} &= \frac{e^2}{2} \lim_{M \rightarrow \infty} \sum_{\alpha\beta\gamma=-M}^M \sum_{i=1}^N \sum_{j=1}^N q_i q_j \frac{1}{|\vec{R}_{\alpha\beta\gamma} - \vec{r}_j + \vec{r}_i|} \\
E_{surf}^{(ew)} &= -\frac{e^2}{2} \lim_{M \rightarrow \infty} \sum_{\alpha\beta\gamma=-M}^M \sum_{i=1}^N \sum_{j=1}^N q_i q_j \frac{1}{V} \int_{V_{\alpha\beta\gamma}} d^3r' \frac{1}{|\vec{R}_{\alpha\beta\gamma} + \vec{r}' - \vec{r}_j + \vec{r}_i|}
\end{aligned} \tag{3}$$

The energy due to the uniform volume charge integration can be more simply expressed by making a change of variables:

$$\begin{aligned}
\vec{r}'' &= \vec{r}' + \vec{r}_i + \vec{R}_{\alpha\beta\gamma} \\
&= \xi'' \vec{a} + \eta'' \vec{b} + \zeta'' \vec{c} \\
\vec{r}_i &= \xi_i \vec{a} + \eta_i \vec{b} + \zeta_i \vec{c} \\
\vec{r}_j &= \xi_j \vec{a} + \eta_j \vec{b} + \zeta_j \vec{c}
\end{aligned} \tag{4}$$

$\xi$ ,  $\eta$ , and  $\zeta$  are the displacements along the  $\vec{a}$ ,  $\vec{b}$ , and  $\vec{c}$  directions, respectively.

With these substitutions,

$$E_{surf}^{(ew)} = \lim_{M \rightarrow \infty} \frac{-e^2}{2} \left\{ \sum_j q_j \sum_i q_i \int_{-M-\frac{1}{2}+\xi_i}^{M+\frac{1}{2}+\xi_i} d\xi'' \int_{-M-\frac{1}{2}+\eta_i}^{M+\frac{1}{2}+\eta_i} d\eta'' \int_{-M-\frac{1}{2}+\zeta_i}^{M+\frac{1}{2}+\zeta_i} d\zeta'' \frac{1}{|\vec{r}'' - \vec{r}_j|} \right\} \tag{5}$$



With a neutral unit cell, the volume charge is zero within the limits  $-A$  to  $+A$ ,  $-B$  to  $+B$ , and  $-C$  to  $+C$ . If this volume is subtracted from the sum, the contributions from the volume charges are limited to integrations over cells which are at the limits of the lattice sums. If the limits are sufficiently large, the volume charge may be approximated by a surface charge concentrated at the limit. For example, with  $M$  sufficiently large,

$$\begin{aligned}
-\sum_i \int_M^{M+\frac{1}{2}+\xi_i} \frac{d\xi''}{|\vec{r}'' - \vec{r}_j|} &\approx -\sum_i q_i \frac{M + \frac{1}{2} + \xi_i - M}{|\vec{r}_{\eta\zeta}'' + M\vec{a} - \vec{r}_j|} \\
&= \frac{-1}{|\vec{r}_{\eta\zeta}'' + M\vec{a} - \vec{r}_j|} \sum_i q_i \xi_i
\end{aligned} \tag{6}$$

$$\vec{r}_{\eta\zeta}'' \equiv \eta''\vec{b} + \zeta''\vec{c}$$

The potential due to the surface charge is found by performing the surface integration over  $\eta''$  and  $\zeta''$ . Neglecting edge and corner effects, the total energy due to the surface charges is

$$\begin{aligned}
E_{surf}^{(ew)} &= \lim_{M \rightarrow \infty} \sum_j q_j \left\{ \int_{-M}^M d\eta \int_{-M}^M d\zeta \left[ \frac{\rho_a}{|\vec{r}_{\eta\zeta}'' + M\vec{a} - \vec{r}_j|} - \frac{\rho_a}{|\vec{r}_{\eta\zeta}'' - M\vec{a} - \vec{r}_j|} \right] \right. \\
&\quad + \int_{-M}^M d\xi \int_{-M}^M d\zeta \left[ \frac{\rho_b}{|\vec{r}_{\xi\zeta}'' + M\vec{b} - \vec{r}_j|} - \frac{\rho_b}{|\vec{r}_{\xi\zeta}'' - M\vec{b} - \vec{r}_j|} \right] \\
&\quad \left. + \int_{-M}^M d\xi \int_{-M}^M d\eta \left[ \frac{\rho_c}{|\vec{r}_{\xi\eta}'' + M\vec{c} - \vec{r}_j|} - \frac{\rho_c}{|\vec{r}_{\xi\eta}'' - M\vec{c} - \vec{r}_j|} \right] \right\}
\end{aligned} \tag{7}$$

$$\rho_a = -\sum_i q_i \xi_i$$

$$\rho_b = -\sum_i q_i \eta_i \tag{8}$$

$$\rho_c = - \sum_i q_i \zeta_i$$

If the surface charge is approximated by a point charge of the appropriate value at each surface lattice point, the integrals can be replaced with two-dimensional lattice sums. The value of the point charge is found to be numerically equal to that of the surface charge. As the limits are taken to infinity, the volume, surface and point charge representations become equivalent.

By inspecting the surface of the finite crystal, it can be seen that the volume charges cancel each other exactly only if the net dipole moment of the unit cell is zero. If the dipole moment is nonzero, then an Ewald summation contains contributions from surface charges with magnitudes given by equation (8) in addition to the direct Coulomb sum of equation (1).

#### IV. Multipole Lattice Sums

In terms of the unnormalized spherical harmonics, the inverse distance between two points  $\vec{r}$  and  $\vec{r}' + \vec{R}_{\alpha\beta\gamma}$  is<sup>6</sup>:

$$\frac{1}{|\vec{r} - \vec{R}_{\alpha\beta\gamma} - \vec{r}'|} = \sum_{k=0}^{\infty} \sum_{n=-k}^k \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{(-1)^l (k+l-m-n)!}{(k+n)!(l+m)!} r^l Y_{lm}^*(\hat{r}) r'^k Y_{kn}^*(\hat{r}') \frac{Y_{k+l,n+m}(\hat{R}_{\alpha\beta\gamma})}{R_{\alpha\beta\gamma}^{k+l+1}} \quad (9)$$

$$Y_{lm}(\hat{r}) \equiv P_l^{|m|}(\cos\theta) e^{im\phi} \quad (10)$$

This expression is only valid if  $r + r' < R_{\alpha\beta\gamma}$ . Because of this, it is necessary to define a sphere about the origin of the MD cell and restrict the application of the multipole expansion to those terms in the lattice sums which come from cells with centers

outside the sphere. This radius must be greater than the longest diagonal of the MD cell to insure the validity of the multipole expansion in all cases. Contributions from ‘near neighbors’ cells inside the sphere are summed directly, so that the total Coulomb energy sum is:

$$E_{coul} = \frac{e^2}{2} \sum_{\alpha\beta\gamma=nn} \sum_{ij=1}^N \frac{q_i q_j}{|\vec{r}_i - \vec{R}_{\alpha\beta\gamma} - \vec{r}_j|} \quad (11)$$

$$+ \frac{e^2}{2} \sum_{\alpha\beta\gamma \neq nn} \sum_{i=1}^N \sum_{j=1}^N q_i q_j \sum_k \sum_n \sum_l \sum_m c_{kn;lm} r_i^l Y_{lm}^*(\hat{r}_i) r_j^k Y_{kn}^*(\hat{r}_j) \frac{Y_{k+l,n+m}(\hat{R}_{\alpha\beta\gamma})}{R_{\alpha\beta\gamma}^{k+l+1}}$$

$$c_{kn;lm} \equiv \frac{(-1)^l (k+l-m-n)!}{(k+n)!(l+m)!} \quad (12)$$

With the multipole moments of the MD cell defined as

$$Q_{lm} \equiv \sum_{i=1}^N q_i r_i^l Y_{lm}(\hat{r}_i) \quad (13)$$

and the first term in equation (11) defined as  $E_{nn}$ , the energy is:

$$E_{coul} = E_{nn} + \frac{e^2}{2} \sum_{kn} \sum_{lm} c_{kn;lm} Q_{lm}^* Q_{kn}^* \sum_{\alpha\beta\gamma \neq nn} \frac{Y_{k+l,n+m}(\hat{R}_{\alpha\beta\gamma})}{R_{\alpha\beta\gamma}^{k+l+1}} \quad (14)$$

The lattice sums can be calculated separately for each combination of  $k+l$  and  $n+m$ . For  $k+l \geq 4$ , these sums are absolutely convergent<sup>11</sup> and can be calculated by the PSM without ambiguity. The indeterminacy in the total energy is contained in the lattice sums with  $k+l < 4$ , and since these sums are at best conditionally convergent other methods must be used for their evaluation.

In all cases but one, terms in the sum which contain combinations of  $k$  and  $l$  with  $k+l < 4$  can be shown to be identically zero. If either  $k$  or  $l$  is equal to zero, then

the charge neutrality of the MD cell insures that  $Q_{00} = 0$ . The inversion symmetry of the Bravais lattice in combination with the parity of spherical harmonics of odd order leads to zero contributions from all odd-valued combinations, including  $k + l$  equal to 1 or 3. The only non-zero terms with  $k + l < 4$  are those with  $k = 1$  and  $l = 1$ . The strength of this term is determined by the collective dipole moment of the charges in the MD cell. As expected, if the dipole moment is zero, then  $Q_{1m}$  is zero and there is no indeterminacy in the overall sum.

In order to evaluate the term with  $k = l = 1$  and nonzero dipole moment, a set of point charges of arbitrary magnitude are added and subtracted at the center of each face of each cell in the lattice. The energy in the MD cell due to these added point charges is zero, which in this case is written

$$0 = \frac{e^2}{2} \sum_{\alpha\beta\gamma=-M}^M \sum_{i=1}^N q_i \sum_{j=a,b,c} \left\{ \frac{\tilde{q}_j}{|\vec{r}_i - \vec{R}_{\alpha\beta\gamma} - \frac{\vec{j}}{2}|} - \frac{\tilde{q}_j}{|\vec{r}_i - \vec{R}_{\alpha\beta\gamma} - \frac{\vec{j}}{2}|} \right\} \quad (15)$$

or

$$\begin{aligned} 0 = & \frac{e^2}{2} \sum_{\alpha\beta\gamma=-M}^M \sum_{i=1}^N q_i \sum_{j=a,b,c} \frac{\tilde{q}_j}{|\vec{r}_i - \vec{R}_{\alpha\beta\gamma} - \frac{\vec{j}}{2}|} \\ & - \frac{e^2}{2} \sum_{\alpha=-M+1}^{M+1} \sum_{\beta\gamma=-M}^M \sum_{i=1}^N q_i \frac{\tilde{q}_a}{|\vec{r}_i - \vec{R}_{\alpha\beta\gamma} + \frac{\vec{a}}{2}|} \\ & - \frac{e^2}{2} \sum_{\beta=-M+1}^{M+1} \sum_{\alpha\gamma=-M}^M \sum_{i=1}^N q_i \frac{\tilde{q}_b}{|\vec{r}_i - \vec{R}_{\alpha\beta\gamma} + \frac{\vec{b}}{2}|} \\ & - \frac{e^2}{2} \sum_{\gamma=-M+1}^{M+1} \sum_{\alpha\beta=-M}^M \sum_{i=1}^N q_i \frac{\tilde{q}_c}{|\vec{r}_i - \vec{R}_{\alpha\beta\gamma} + \frac{\vec{c}}{2}|} \end{aligned} \quad (16)$$

By combining the contributions from the positive and negative charges at each common lattice point, a single lattice sum plus a number of surface terms are created:

$$\begin{aligned}
0 = & \frac{e^2}{2} \sum_{\alpha\beta\gamma=-M}^M \sum_{i=1}^N q_i \sum_{j=a,b,c} \left\{ \frac{\tilde{q}_j}{|\vec{r}_i - \vec{R}_{\alpha\beta\gamma} - \frac{\vec{j}}{2}|} - \frac{\tilde{q}_j}{|\vec{r}_i - \vec{R}_{\alpha\beta\gamma} + \frac{\vec{j}}{2}|} \right\} \\
& - \frac{e^2}{2} \sum_{i=1}^N q_i \sum_{\beta\gamma=-M}^M \left\{ \frac{\tilde{q}_a}{|\vec{r}_i - \vec{R}_{-M-1,\beta\gamma} + \frac{\vec{a}}{2}|} - \frac{\tilde{q}_a}{|\vec{r}_i - \vec{R}_{M\beta\gamma} + \frac{\vec{a}}{2}|} \right\} \\
& - \frac{e^2}{2} \sum_{i=1}^N q_i \sum_{\alpha\gamma=-M}^M \left\{ \frac{\tilde{q}_b}{|\vec{r}_i - \vec{R}_{\alpha-M-1,\gamma} + \frac{\vec{b}}{2}|} - \frac{\tilde{q}_b}{|\vec{r}_i - \vec{R}_{\alpha M\gamma} + \frac{\vec{b}}{2}|} \right\} \\
& - \frac{e^2}{2} \sum_{i=1}^N q_i \sum_{\alpha\beta=-M}^M \left\{ \frac{\tilde{q}_c}{|\vec{r}_i - \vec{R}_{\alpha\beta-M-1} + \frac{\vec{c}}{2}|} - \frac{\tilde{q}_c}{|\vec{r}_i - \vec{R}_{\alpha\beta M} + \frac{\vec{c}}{2}|} \right\} \quad (17)
\end{aligned}$$

The last three terms contain point charges spaced uniformly on the surfaces of the finite crystal. Representing these terms by  $-E_{surf}^{mp}$  and performing a multipole expansion on the terms in the lattice which are not near neighbors,

$$\begin{aligned}
0 = & \frac{e^2}{2} \sum_{\alpha\beta\gamma=nn} \sum_{i=1}^N q_i \sum_{j=a,b,c} \left\{ \frac{\tilde{q}_j}{|\vec{r}_i - \vec{R}_{\alpha\beta\gamma} - \frac{\vec{j}}{2}|} - \frac{\tilde{q}_j}{|\vec{r}_i - \vec{R}_{\alpha\beta\gamma} + \frac{\vec{j}}{2}|} \right\} - E_{surf}^{mp} \\
& + \frac{e^2}{2} \sum_{kn} \sum_{lm} c_{kn;lm} Q_{lm}^* \left\{ \sum_{j=a,b,c} \tilde{q}_j \left( \frac{r_j}{2} \right)^k (Y_{kn}^*(\hat{j}) - Y_{kn}^*(-\hat{j})) \right\} \\
& \times \sum_{\alpha\beta\gamma \neq nn} \frac{Y_{k+l,n+m}(\hat{R}_{\alpha\beta\gamma})}{R_{\alpha\beta\gamma}^{k+l+1}} \quad (18)
\end{aligned}$$

Referring to the first term in this equation as  $\tilde{E}_{nn}$  and the expression in brackets in the multipole term as  $\tilde{Q}_{kn}^*$ , this equation becomes:

$$0 = \tilde{E}_{nn} - E_{surf}^{mp} + \frac{e^2}{2} \sum_{kn} \sum_{lm} c_{kn;lm} Q_{lm}^* \tilde{Q}_{kn}^* \sum_{\alpha\beta\gamma \neq nn} \frac{Y_{k+l,n+m}(\hat{R}_{\alpha\beta\gamma})}{R_{\alpha\beta\gamma}^{k+l+1}} \quad (19)$$

Values for  $\tilde{q}_a$ ,  $\tilde{q}_b$ , and  $\tilde{q}_c$  are determined by setting  $\tilde{Q}_{1m} = -Q_{1m}$ . The resulting values for the compensating charges are

$$\tilde{q}_a = - \sum_{i=1}^N q_i \xi_i$$

$$\begin{aligned}
\tilde{q}_b &= -\sum_{i=1}^N q_i \eta_i \\
\tilde{q}_c &= -\sum_{i=1}^N q_i \zeta_i
\end{aligned} \tag{20}$$

Compensating charges for the unit cells of Figure 1 are shown in Figure 2.

In an orthorhombic lattice the compensating charges are proportional to the dipole moments of the unit cell. In triclinic lattices the values are proportional to the projection of the total dipole moment along the lattice vectors. Using these values for the compensating charges, the dipole moment for the MD cell can be equated to an expression containing terms which represent a surface charge, a near neighbor sum, and lattice sums which are all absolutely convergent:

$$\begin{aligned}
& \frac{1}{2} \sum_{m=-1}^1 \sum_{n=-1}^1 c_{1n;1m} Q_{1m}^* Q_{1n}^* \sum_{\alpha\beta\gamma \neq nn} \frac{Y_{2,n+m}(\hat{R}_{\alpha\beta\gamma})}{R_{\alpha\beta\gamma}^{k+l+1}} \\
&= \tilde{E}_{nn} + \frac{1}{2} \sum_{lm} \sum_{kn} c_{kn;lm} Q_{lm}^* \tilde{Q}_{kn}^* \sum_{\alpha\beta\gamma \neq nn} \frac{Y_{k+l,n+m}(\hat{R}_{\alpha\beta\gamma})}{R_{\alpha\beta\gamma}^{k+l+1}} - E_{surf}^{mp}
\end{aligned} \tag{21}$$

Here the sums on the RHS are restricted to values of  $k$  and  $l$  for which  $k + l \geq 4$ .

When this expression is inserted into the original Coulomb sum, the required form for the total electrostatic energy is obtained.

$$\begin{aligned}
E_{coul} &= E_{nn} + \tilde{E}_{nn} - E_{surf}^{mp} \\
&+ \frac{1}{2} \sum_{lm} \sum_{kn} c_{kn;lm} Q_{lm}^* (Q_{kn}^* + \tilde{Q}_{kn}^*) \sum_{\alpha\beta\gamma \neq nn} \frac{Y_{k+l,n+m}(\hat{R}_{\alpha\beta\gamma})}{R_{\alpha\beta\gamma}^{k+l+1}}
\end{aligned} \tag{22}$$

The distance from the original MD cell to the surface charges can be taken to be very large compared to the cell dimensions. In this limit the point charges at the

summation limits can be well approximated as surface charges with values  $\rho_a = \tilde{q}_a/A_{bc}$ ,  $\rho_b = \tilde{q}_b/A_{ac}$  and  $\rho_c = \tilde{q}_c/A_{ab}$ .  $A_{ab}$  is the area of the MD cell face defined by lattice vectors  $\vec{a}$  and  $\vec{b}$ .  $A_{ac}$  and  $A_{bc}$  are defined similarly.

If the energy of the system is taken as

$$E_{mp} \equiv E_{coul} + E_{surf}^{mp} \quad (23)$$

then all of the lattice sums are absolutely convergent and the forces generated by  $E_{mp}$  are periodic with the lattice. Because of this, the value of the energy is not affected by the definition of the unit cell. In fact,  $E_{mp}$  is the same as the Ewald energy if the same lattice limits are used in both cases, and the surface charge distributions generated by each method are identical.

## V. Calculations

Analytically, the multipole and Ewald methods produce identical numerical results when applied to a given MD cell. The choice of which to use in dynamical simulations may be made by considering the speed and accuracy of the algorithms available for each of these methods.

The multipole expressions for energy and force were incorporated in a rather simple way into energy and force subroutines for molecular dynamics simulations. The near neighbor interactions are calculated directly, and the planewise summation method is used to calculate the lattice sums for the long-range Coulomb interactions. The resulting algorithm includes a number of calculations proportional to  $N^2$  due to the near neighbor terms. The multipole calculations also contain a number of terms proportional to  $N$  as well as a number of calculations proportional to the fourth power of the highest order

multipole index included in the sums.

The multipole expansion is valid for cells with centers more than the maximum MD cell diagonal from the the origin, but if this distance is used as a cutoff radius the multipole terms will converge very slowly. For maximum efficiency, the number of direct calculations within a given cutoff radius must be weighed against the number of terms in the multipole expansion which are required to achieve a given accuracy.

In addition to the error associated with truncation of the multipole expansion, additional numerical errors arise from the computation of the lattice sums using the planewise summation. Because this method uses Fourier transforms to replace multipole lattice sums with more rapidly converging series, it can be applied only to sums over a complete lattice. In order to use the planewise method as part of a multipole method, the multipole sums are written:

$$\sum_{\alpha\beta\gamma \neq nn} \frac{Y_{lm}(\hat{R}_{\alpha\beta\gamma})}{R_{\alpha\beta\gamma}^{l+1}} = \sum'_{\alpha\beta\gamma} \frac{Y_{lm}(\hat{R}_{\alpha\beta\gamma})}{R_{\alpha\beta\gamma}^{l+1}} - \sum'_{nn} \frac{Y_{lm}(\hat{R}_{\alpha\beta\gamma})}{R_{\alpha\beta\gamma}^{l+1}} \quad (24)$$

The primes denotes sums over all lattice points except the origin. The sum over the complete lattice can be calculated using the planewise summation method for each value of  $l$  and  $m$ . The terms in the sum over near neighbors are then calculated separately and subtracted from the planewise result.

The subtraction of two lattice sums which are nearly equal in value tends to exaggerate the numerical errors introduced with the planewise summation method. A truncation error in the planewise sums will produce errors relative to the lattice sum over all space, which is usually several orders of magnitude larger than a sum which is restricted to lattice points outside a cutoff radius.



For purposes of comparison, subroutines were also written for calculation of the Coulomb energy and forces with the Ewald method. The free parameter in the Ewald summations was set to  $\alpha = \sqrt{\pi}/a$ ,  $a$  being the lattice constant. This definition of  $\alpha$  is used for all calculations described here, with the result that for non-cubic cells the rate of convergence depends on the ratios of the lattice constants.

Error estimates for various sets of computational parameters required to obtain a specified error tolerance in the multipole and Ewald methods are listed in Table 1. The lattice sums for the planewise and Ewald summations include all terms with the absolute value of any summation index less than or equal to  $M_{PSM}$  and  $M_{ew}$ , respectively.  $\mu$  is the maximum multipole order included in the multipole sums.

In order to check the relative efficiency of the two methods, a number of computer runs were made with each force routine for the same unit cell. Each run included 81 force and 3 energy calculations. The parameters used were  $M_{ew}=3$ ,  $\mu=14$  and  $M_{PSM}=7$  for an expected relative error of  $10^{-6}$ . Results are shown in Figure 3. More details are found in reference 12.

## V. Discussion

The multipole subroutine described here includes a number of calculations proportional to  $N^2$  because of the direct terms in the lattice summation. These terms are simpler than those in the Ewald summation, and total run time is less for systems containing moderately large numbers of atoms. There are many approaches to improving the speed of the fast multipole algorithm but these are not pursued here. As implemented, the multipole routine is faster than the Ewald routine but not overwhelmingly so. The relative simplicity of the Ewald formulation makes the Ewald method easier to

program and debug.

In addition to the Coulomb interaction for ionic crystals, it is often desirable in simulations to calculate the energy and forces from interactions which are proportional to any negative power of the separation distance. The Ewald method was extended by Nijboer and deWette<sup>2</sup> to include this type of lattice sum, and Williams<sup>13</sup> later extended their methods to allow multiple atoms in a unit cell. These techniques give formulas which can be used to perform fast summation of potentials and forces which would otherwise converge very slowly, such as the  $r^{-4}$  dipole-charge interaction commonly encountered in ionic models and the  $r^{-6}$  Van der Waals or dispersion interaction. The formulas become progressively more complicated as the reciprocal power increases, and it is common to use a cutoff radius to calculate these potentials rather than utilize the rapidly converging formulation.

Incorporation of interaction potentials of the form  $r^{-n}$  into a multipole method presents some difficulties. The multipole separation used for the Coulomb potential cannot be used for the higher power terms; since these terms do not satisfy Laplace's equation they cannot be constructed from linear combinations of the solutions to that equation. The multipole character of the summations could be preserved by separating the lattice sums and particle coordinates through application of a three-dimensional Taylor series expansion. These lattice sums could in principle be evaluated with a number of operations proportional to  $N$  by planewise summation and then differentiated to obtain the terms which would be included in the multipole sums.

An alternative approach for including the higher-power terms in a multipole method is found by considering these terms in light of their physical origins. The  $r^{-4}$  term is

generally considered to be a charge-dipole interaction, while the  $r^{-6}$  terms usually arise from an induced dipole-dipole interaction. If each atom is assigned a polarizability, then the dipole moment induced in each atom will be proportional to the electric field at that atom. The field at each atom is routinely obtained as part of the force calculation. The charge-dipole interaction could then be calculated directly for near neighbors and through an additional multipole sum for the long-range contributions. The corrections to the electric field at each atom would in turn cause corrections in the atomic dipole moments, and repetition of this procedure would be necessary until a specified degree of self-consistency is obtained. At each step the only corrections are to the multipole moments of the unit cell; the lattice sums remain unchanged throughout the self-consistency routine.

The direct calculation of dipole interactions through the multipole method would have a number of advantages. All of the electrostatic forces due to dipole interactions are included automatically; the  $r^{-4}$  and  $r^{-6}$  potentials, for instance, need not be considered separately. Using fast multipole techniques, it is possible to construct algorithms which include all of the electrostatic forces to any required degree of accuracy with a number of calculations proportional to  $N$ . The short-range forces would be calculated in the last step of the fast multipole procedure and would also require a number of calculations proportional to  $N$ . The method could readily be extended to include quadrupole and higher order interactions if required.

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## References

1. See, for example, J.C. Slater, "Insulators, Semiconductores, and Metals" (McGraw Hill, New York, 1967), chapter 9.
2. B. R. A. Nijboer and F. W. de Wette, *Physica* **23**, 309 (1957).
3. M. J. L. Sangster and M. Dixon, *Adv. Phys.* **25**, 247 (1976).
4. N. Karasawa and W. A. Goddard, *J. Phys. Chem.* **93**, 7320 (1989).
5. B. R. A. Nijboer and F. W. de Wette, *Physica* **24**, 422 (1958).
6. B. R. A. Nijboer and F. W. de Wette, *Physica* **24**, 1105 (1958).
7. V. Massidda and J. A. Hernando, *Physica* **101B**, 159 (1980).
8. V. Massida, *Physica* **95B**, 317 (1978).
9. E. Evjen, *Phys. Rev.* **39**, 675 (1932).
10. L. Greengard and V. Rokhlin, *J. Comp. Phys.* **73**, 325 (1987).
11. C. A. Scholl, *Proc. Phys. Soc.* **87**, 897 (1966).
12. M. J. Love, PhD thesis, 1993, unpublished.
13. D. E. Williams, *Acta Cryst. A* **27**, 452 (1971).

Table 1.

Parameters for error tolerances for multipole and Ewald methods.

$\epsilon_{coul}$	n=1.5		n=2		Ewald
	$\mu$	$M_{psm}$	$\mu$	$M_{psm}$	$M_{Ew}$
$10^{-4}$	16	6	8	4	2
$10^{-5}$	20	8	12	6	3
$10^{-6}$	>20	>8	14	7	3
$10^{-7}$	>20	>8	16	8	4

### Figure Captions

Figure 1.

Two equivalent unit cells for tetragonal  $ZrO_2$ . Cross-hatched circles are  $Zr^{4+}$  ions and open circles are  $O^{2-}$  ions.  $P$  is the dipole moment of the unit cell.

Figure 2.

Addition of compensating charges which result in zero dipole moments for the unit cells of Figure 1. Parallel hatched circles are the compensating charges.

Figure 3.

Computer run times for various numbers of atoms per unit cell. Forces are calculated by the Ewald method (circles) or by the planewise summation method (triangles).